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Ohmic Heating of Composite Candidate Graphite-Fiber/Coating Combinations

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Summary

Graphite fibers were heated in a vacuum to test the adhesion of deposited films at elevated temperatures. Copper-clad fibers and fibers with bilayer coatings were resistance heated by a direct-current power supply. Where possible, peak temperatures were measured with a long-focal-length optical pyrometer. Fiber surface wetting or nonwetting behavior could be clearly observed after this relatively quick and simple procedure. These results are discussed in the context of creating composites of graphite fibers in a copper matrix.

Introduction

Copper matrix composites reinforced with high-modulus graphite fibers are candidate space radiator materials that offer the intriguing property of allowing the directional thermal conductivity and the coefficient of thermal expansion to be tailored within a given range (ref. 1). However, graphite fibers can fail in copper matrixes because of the lack of adhesion between copper and the graphite surface, evidenced by the "nonwetting" or "beading up" behavior of pure copper on graphite and by the formation of voids at the copper/graphite interface.

Three general methods of improving the fiber-to-matrix bonding can be cited: fiber surface modification, matrix alloying additions, and interfacial bond layers. Although conceptually distinct in approach, in practice the three methods may produce similar results. For example, if the composite is exposed to moderately high temperatures, diffusion of an interfacial bond layer out into the matrix might be of concern. The resulting final distribution of bond layer material could resemble the distribution resulting from an initially dilute copper alloy.

In the early 1970's Mortimer and Nicholas investigated improving copper bonding to graphite and vitreous carbon by alloying the copper with small amounts of several active metals (ref. 2). The same authors investigated pure copper wetting of various carbides as well (ref. 3). Recently, renewed interest in the copper-to-graphite bonding problem has been evidenced (ref. 4).

This report presents a simple, relatively quick indicator test of the adhesion of a metal film to a graphite fiber. The actual

fibers of interest were tested to more closely relate the results to composite materials. Films of copper with and without active metal bond layers were used for comparison.

Experimental Procedure

Graphite fibers of technological interest were used for this experiment. The pitch-based, $\sim 10\text{-}\mu\text{m}$ -diameter fibers are composed primarily of longitudinally oriented, folded graphitelike sheets with a striated fiber surface (refs. 5 and 6). The uncoated fibers have a quoted tensile strength of 2.37 GPa (350 ksi) (ref. 7). The fibers were obtained coated with either pure copper (ref. 8), a tungsten bond layer followed by copper (ref. 9), or a thin titanium bond layer followed by copper (ref. 10). No further treatment was performed on the supplied fibers before testing, and care was taken not to directly handle the fibers during mounting.

Individual fibers, or small bundles of fibers when necessary, were mounted between electrical contacts for resistance heating with a direct-current power supply. Within limits, the fiber resistance could be modified by varying the length of fiber used. Less than 20 V were needed for individual fibers, and no more than 5 A were required for a fiber bundle. The variable power supply was run in current-limiting mode for the best manual control.

Resistive self-heating of the carbon fibers, which is reminiscent of the earliest light bulbs, has the advantage that no system components other than the fiber become significantly heated. In the experiment, a temperature gradient was established between the center and ends of the carbon fiber because the mounting points tended to serve as heat sinks. A long-focal-length, "disappearing-filament" optical pyrometer was used to estimate temperatures (ref. 11). By crossing the pyrometer filament with the hottest, middle portion of the carbon fiber in the pyrometer field of view, we could obtain an indication of fiber temperature when the crossing points from the filament to the fiber disappeared. The highest temperatures used were not far above or below 1356 K, the melting temperature of copper.

The small vacuum chamber employed was constructed entirely of ultra-high-vacuum components. A single zeolite-filled cryogenic absorption pump with thermocouple gauging evacuated a six-way cross with a nominal 1.5-in.-diameter internal clearance to below 10 mtorr. Conflat-flanged Pyrex

windows allowed the optical pyrometer to view the fibers. Fiber samples were mounted on a multipin vacuum electrical feed-through, allowing several samples to be tested during one pump-down of the vacuum system. No measurable rise in pressure was detected on the thermocouple vacuum pressure gauge when the fibers were heated.

Coated fibers were examined both before and after heating with a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS) (ref. 12).

Results

Figure 1 shows copper-clad fibers without a bond layer after vacuum heating. These $\sim 10\text{-}\mu\text{m}$ -diameter fibers, which were coated with an approximately $20\text{-}\mu\text{m}$ -thick copper film, exhibited significantly lower electrical resistance when the copper was uninterrupted. Upon heating to or near to the copper melting temperature, the copper film would suddenly become discontinuous, the bare fiber would jump in temperature (constant current power supply), and the melted copper would form a bead on the fiber. On fibers without a bond layer, the copper formed nearly spherical beads, exhibiting large contact angles with the graphite.

The copper/titanium films deposited on graphite fibers displayed a striking, nodular morphology before heating (fig. 2(a)). Individual fibers were difficult to separate for mounting. A bundle of fibers, self-heated to catastrophic failure, showed mixed wetting behavior. Both high-contact-angle beading of the copper on otherwise bare fibers and low-contact-angle clumps could be observed on the heated bundle (fig. 2(b)). Fibers on which only the titanium bond layer had been deposited were also supplied (fig. 3). EDS mapping as well as spot-mode EDS spectra taken on and between the visibly patchy surface material, showed the patches to be titanium.

For a copper/tungsten film, the beads formed during heating revealed contact angles smaller than 90° (fig. 4(a)). Revealed as well was a tungsten bond layer with a convoluted structure. The tungsten bond layer itself was thick enough to exhibit mechanical failure after heating (fig. 4(b)).

Discussion

This work was undertaken to test copper adhesion to high-modulus graphite fibers with and without bond layers deposited on the fibers. These thin-film heating results may provide early indicators of the behavior of composites that incorporate such fibers into a copper matrix.

Some theoretical work has related contact-angle experiments to actual composite fabrication (ref. 13). Young concluded that for complete infiltration of fiber mats by a matrix material, the

contact angle between the matrix and fiber must be less than 90° (i.e., at least partially wetting). The difficulties in producing satisfactory composite panels from pure copper and unmodified graphite fibers have been documented (ref. 1). The expected behavior of a proposed composite may be indicated by the difference between the high contact angle of pure copper on graphite fibers versus the acute contact angles of the copper/tungsten or copper/titanium systems.

The titanium-only coated fibers exhibited incomplete surface coverage by the thin titanium bond layer, and the copper/titanium fiber samples were created under the same titanium-deposition conditions. The discontinuous copper coverage after fiber heating might be associated with an initially uneven titanium bond layer distribution on the copper/titanium fiber surfaces. Areas of high contact angle between the metal and fiber then may be due to an initial local lack of the titanium bond layer. Whether due to an initially patchy titanium coating or to an intrinsic property of the combination of materials, the patchy copper coverage on this set of fibers was revealed by a simple, relatively quick self-heating test.

The copper/tungsten fiber images after heating (fig. 4(a)) showed the expected wetting of tungsten surfaces by copper, despite the unusual, corallike tungsten morphology. The tungsten layer itself proved thick enough to delaminate, however (fig. 4(b)). A thinner coverage of the relatively dense tungsten, if possible, might enhance copper adhesion without adding excessive mass to the composite. Again, the relatively simple self-heating test of these fibers flagged this potential area of investigation.

The ohmic heating of different fiber samples can allow one to quickly compare properties. Quantitative conclusions are more problematic. The exact temperature gradient across the fiber cannot be determined unless the support-post temperature rise is known in addition to the peak measured fiber temperature. The temperature can be controlled manually in the slowly changing initial heating. Fast changes, such as the separation of a conductive metal coating, which shunts the entire heating current into the fiber, may prove too rapid even for relatively fast temperature controllers. Also, the method is only easily applied to conductive fibers. Small-diameter fibers present an additional handling difficulty. It is hard to mount them reproducibly for good electrical contact without fiber damage. This test method does have the advantage that the fibers alone reach significant temperatures, reducing the likelihood of contaminants coming from the furnace or vacuum chamber walls. In addition, few system components are required, primarily a power supply and a small vacuum system or a controlled atmosphere chamber.

Conclusions

The behavior difference between heated copper coatings on graphite fibers with and without bond layers can be quickly and relatively easily demonstrated with a simple

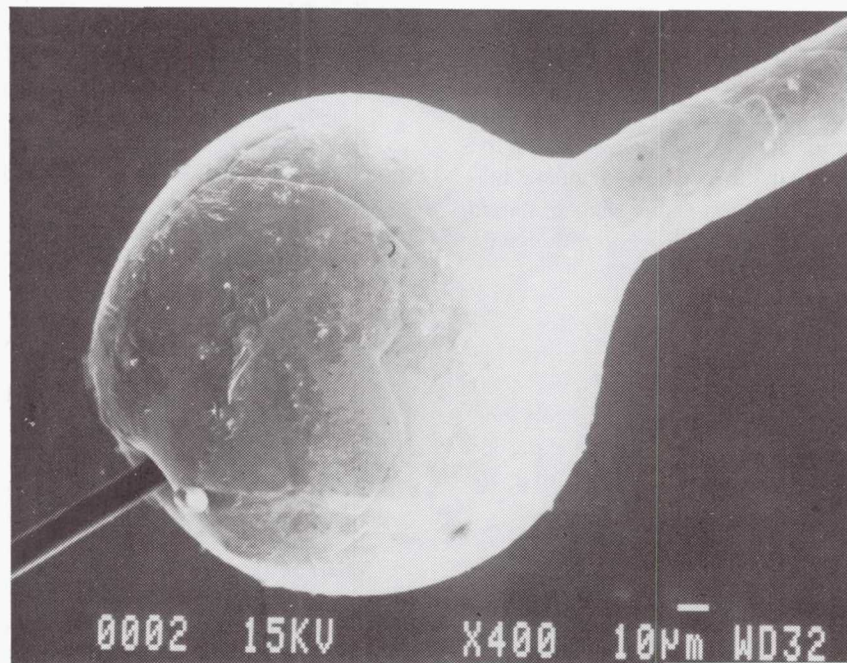
hardware setup. Investigating fibers of technological interest avoids the application of conclusions from research on other forms of carbon. Differences between coatings on individual fibers can flag questions of importance for creating test panels that use the films. In the present study the need for a thinner tungsten bond layer and for a more uniform coverage of the titanium bond layer was revealed. On the basis of film behavior during the heating of copper films on graphite fibers with and without titanium or tungsten bond layers, either bond layer element should improve the adhesion between copper matrices and carbon reinforcement fibers when it is properly applied.

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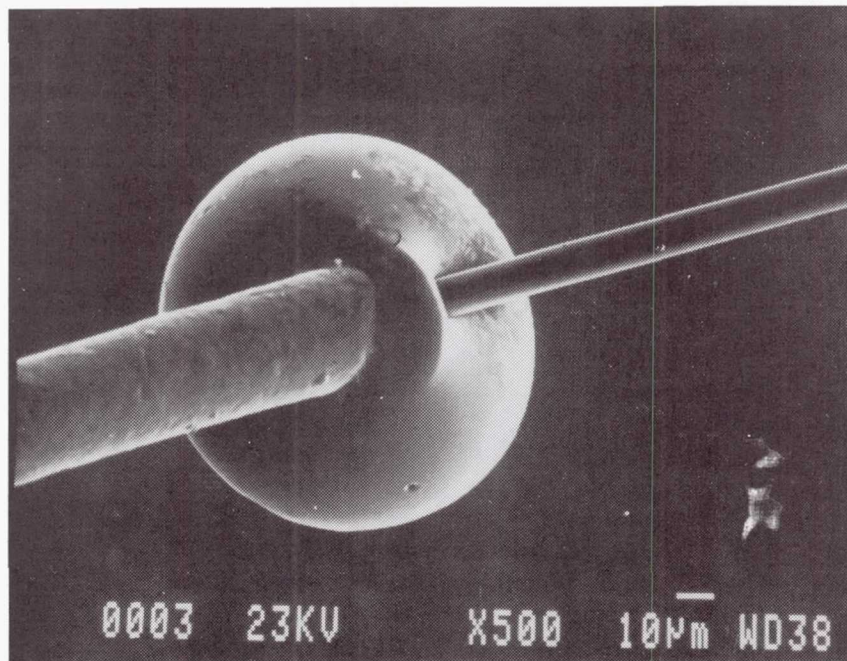
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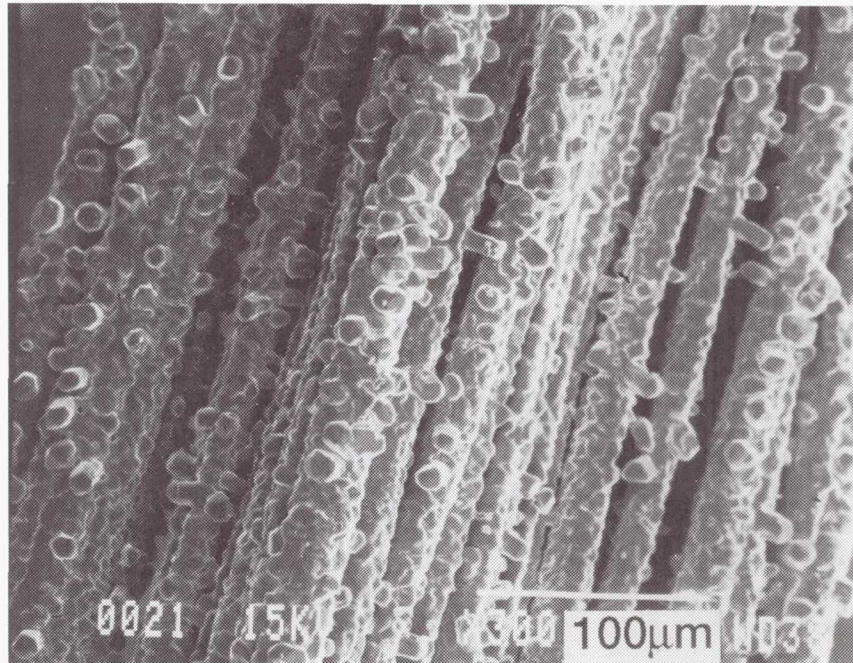


(a) Note high contact angle. Beam voltage, 15 kV.

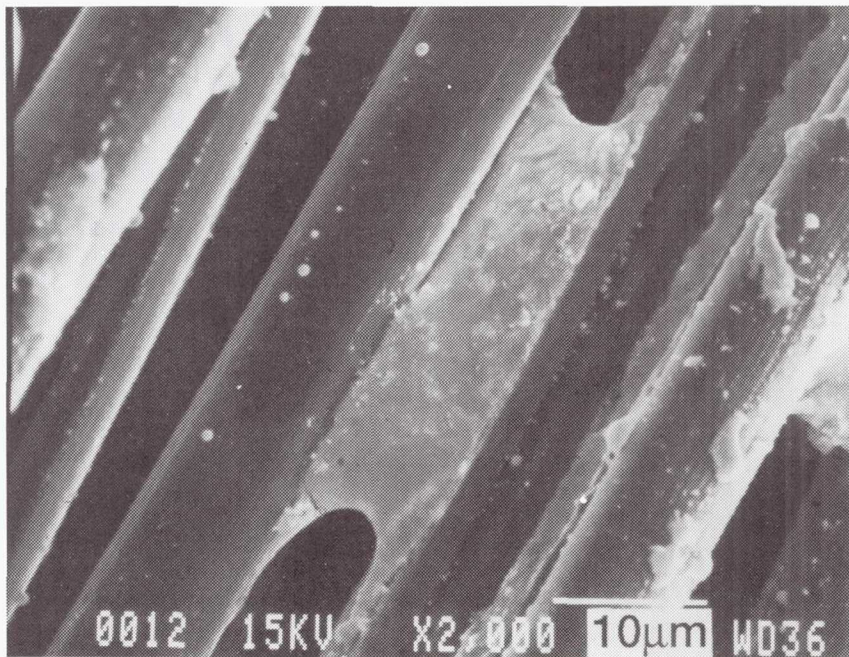


(b) Note apparent effect of gravity on symmetry of bead. Beam voltage, 23 kV.

Figure 1.—Scanning electron micrographs of copper beads formed after self-heating of copper-clad graphite fibers without bond layer.



(a) Fibers in as-received condition.



(b) Fiber bundle heated to catastrophic failure. Note that both copper beading behavior and acute contact angles formed between metal and fibers.

Figure 2.—Scanning electron micrographs of copper/titanium on graphite fibers. Beam voltage, 15 kV.

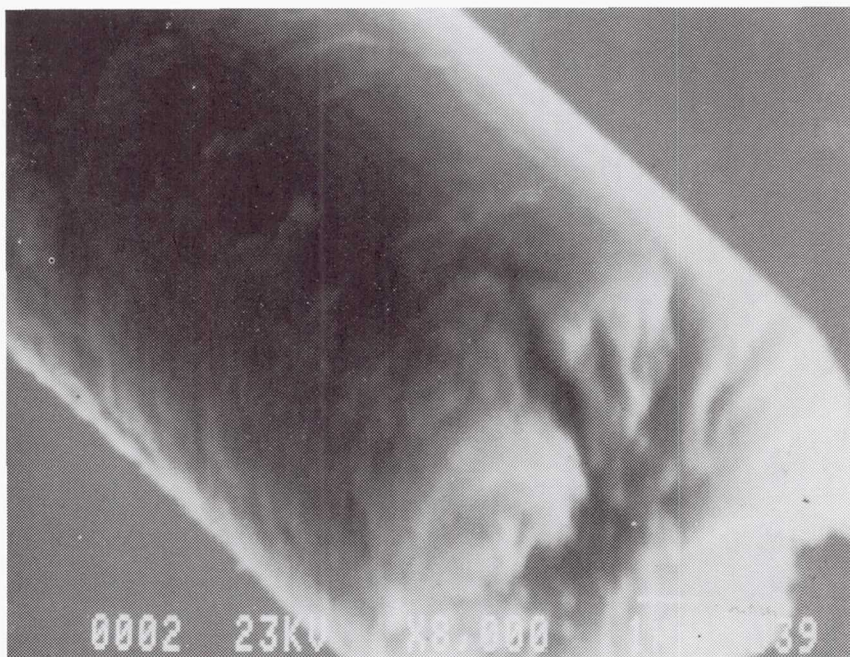
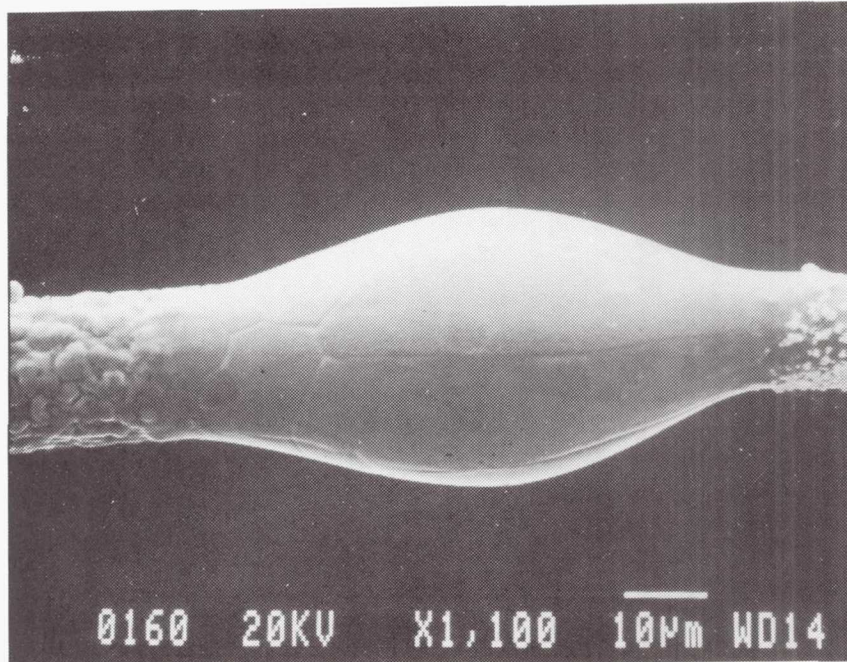
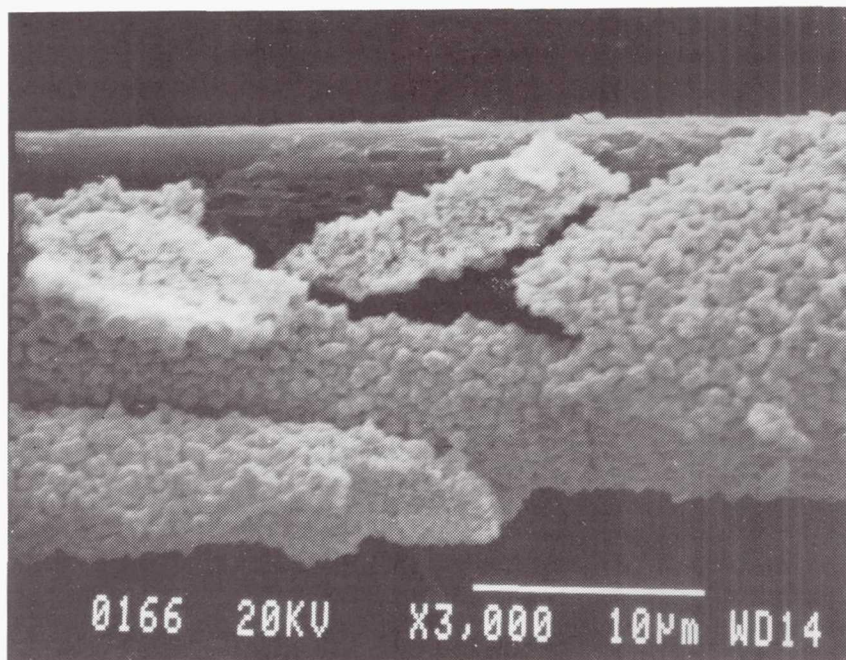


Figure 3.—Scanning electron micrograph of as-supplied titanium film on graphite fiber. Visibly patchy film indicates inhomogeneous titanium distribution (via energy dispersive x-ray spectrometer). Beam voltage, 23 kV.



(a) Melted copper region to right in image; original, as-received surface texture at left edge of image; and partial exposure of tungsten bond layer at right edge of image..



(b) Tungsten bond layer entirely exposed (no copper). Note the pieces of delaminated tungsten bond layer.

Figure 4.—Self-heated copper/tungsten coating on graphite fiber. Beam voltage, 20 kV.

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